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Inhomogeneous Coarse-Graining of Polymers and Polymer/Metal Interfaces

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A "molecule-fixed" inhomogenous coarse-graining scheme for bisphenol-A polycarbonate (BPA-PC) represents the first attempt to use both atomistic and coarse-grained resolution simultaneously to model a specific polymer [Abrams, et. al, *Phys. Rev. E* **67**:021807]. In this model, non-terminal BPA-PC chemical repeat units are each represented by four spherical beads, corresponding to four comonomeric functional groups. At chain ends, the terminal carbonate groups are represented atomistically. Interactions between the respective beads and a nickel surface were parameterized using *ab initio* calculations. This model is reviewed here, and we discuss its application in molecular dynamics simulations of dense liquids of BPA-PC adjacent to (111) nickel surfaces. We observe that the structure of the liquid near the wall is sensitively affected by (a) the strong attraction of the chain ends to the surface, and (b) the strong orientational dependence of this attraction. On scales larger than the bulk unperturbed radius of gyration, the solid/liquid interface has two distinct liquid layers: in the innermost layer near the wall, most chains have both ends adsorbed, while in the outermost layer, most chains have a single end adsorbed. Chain conformations are generally flattened in the innermost layer and stretched in the outermost layer. The overlap between these two layers is more diffuse in the case of the longer chains. Because the transferability of "molecule-fixed" inhomogeneous models to other polymer/metal interface systems seems unlikely, we conclude by speculating on the more general notion of "domain-fixed" inhomogenously resolved models for polymeric systems. These speculations are based upon preliminary simulations of a domain-fixed dual-resolution model of liquid methane.

1 Introduction

Simulation of specific polymer systems has recently been greatly advanced by employing systematically derived coarse-grained molecular models.[1–4] These models vary in the details of their development and implementation, yet all seek to construct particle- or lattice-based chain-like objects whose constituents represent at most a few chemical repeating units of any specific polymer. This is meant to circumvent the great difficulty in producing equilibrated samples of atomically-resolved polymers due to the $O(10)$ orders of magnitude spread between the resolution required in time for standard atomistic molecular dynamics (MD) simulation (10^{-15} s) and the slow molecular relaxation times ($\sim 10^{-5}$ s) which must be achieved. Monte Carlo simulation fares no better as an alternative approach, especially in dense multimolecular systems, because local moves are constrained to impractically small values by steep bonded potentials, and enormous numbers of successful moves have to accumulate in order to move chain sections larger than a repeat unit or so. Integrating out these fast motions, or put another way, averaging over their underlying steep potentials, allows us in principle to construct models that can produce equilibrated configurations with relatively much less computational effort.

Coarse-graining aims to guarantee that the chain conformations in a simulation sample represent true equilibrium conformations of the specific polymer considered. A central

feature of coarse-graining is that the models retain only as much unique and relevant information as needed about the specific polymer(s) under investigation, using significantly fewer degrees of freedom (*i.e.*, particles) than required for full atomistic detail. The coarsened degrees of freedom must be constrained within ensembles of configurations which represent an appropriate average over the microscopic atomic-scale potential energy surface of the fully resolved system. Once an equilibrated sample at the coarse-grained level is generated using an appropriate simulation technique which samples these ensembles, atomic details can be inverse mapped to study atomic-scale properties and processes on then appropriately short length and time scales.[5]

Our focus in recent years has been developing a method for coarse graining melts of bisphenol A-polycarbonate (BPA-PC)[6,5,7–9] (Fig. 1). BPA-PC not only provides a challenging test case for this type of modeling, it is also by far the most utilized and intensively studied variety of polycarbonate, thanks to its many valuable material properties, such as high impact strength, ductility, glass transition and melting temperatures[10]. Coarse-grained simulations can potentially fill a gap that now exists between traditional atomistic simulation and experiments, by addressing longer length and time scales, allowing one to test hypotheses regarding inter- and intramolecular interplay in packing and entanglement that are otherwise more difficult to approach.

Metal surfaces are particularly relevant for industrial processing of polycarbonate, and indeed many other synthetic polymers. The interplay between specific local adsorption of organic chain segments and the much larger scale chain conformations is difficult to capture with traditionally simple molecular and atomic-scale models. Our contributions so far have presented a technique involving appropriate coupling of information from detailed *ab initio* calculations of small molecule/surface interactions into coarse-grained molecular dynamics simulations of liquids of comparatively much larger macromolecules.[8,11] For the purposes of these proceedings, we are particularly interested in understanding the adhesion behavior of BPA-PC liquids next to crystalline nickel surfaces, and how chain length affects this behavior.

Polymer/surface interactions are especially challenging to capture with coarse-grained models due to the specificity of the interactions for various comonomeric groups in complicated polymers, such as BPA-PC. The challenge lies in the fact that the averaging over the microscopic potential energy surface which gives coarse-grained potentials for bulk BPA-PC is strictly not valid when chains strongly interact with a surface, which is the case for the BPA-PC/Ni. For this reason, we have constructed a dual-resolution representation of BPA-PC– combining both coarse-grained and atomic-scale resolution in the same representation – in order to capture as much of the specificity of the polymer/surface interaction as possible, while maintaining the computational advantages of coarse-graining[11]. In a recent publication, we presented the details of this dual-resolution scheme (which are briefly recapitulated below) and presented preliminary results on the structure of a 10-repeat-unit BPA-PC liquid near a Ni (111) surface[11]. Here, we expand upon the results presented in Ref.[11] to consider the effects of longer chains on the structure of the melt near the surface.

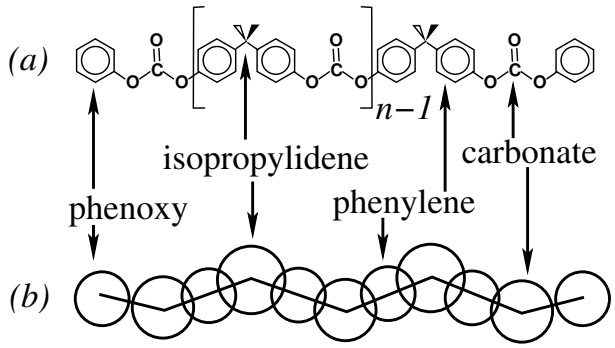

Figure 1. (abrams/*a*) Schematic representation of the structure of bisphenol A-polycarbonate. The relevant comonomeric groups are labeled. The nth repeat unit is outside the brackets because we distinguish *terminal* carbonate groups from *internal* carbonate groups in the dual-resolution model. (*b*) Schematic representation of the 4:1 coarse-grained model of BPA-PC, detailed in Ref.[9].

2 The "Molecule-Fixed" Dual-Resolution Coarse-Grained Model of BPA-PC

2.1 The 4:1 Single-Resolution Model

For a complete presentation of the dual-resolution model of BPA-PC and simulation techniques, we refer the reader to Ref.[11]. Fig. 1 shows the chemical structure of a BPA-PC molecule composed of n repeat units. The repeat unit is constructed of four sequential subunits: a phenylene, an isopropylidene, a second phenylene, and a carbonate. The ends of a BPA-PC molecule are phenyls connected to carbonates. Because the terminal phenyls are each bound to an oxygen of their respective carbonate, we term these "phenoxy" ends. Other end groups apart from phenoxies are currently being considered in work that is not discussed here.[12]

The 4:1 coarse-grained representation of BPA-PC[9] replaces the atomic structure of the repeat unit, which contains 33 atoms, with four spherical beads, two of which are centered on the backbone carbons of the carbonate and isopropylidene groups, respectively. The other two beads "float" at a fixed distance along a line connecting adjacent pairs of carbonate-isopropylidine ("c"–"i"), and are meant to roughly occupy space ascribed to the phenylene ("p")groups. The diameters of these beads are chosen so that they have proper relative sizes and as a group occupy the proper van der Waals excluded volume of the repeat unit.[13] These diameters parameterize repulsive pairwise Weeks-Chandler-Andersen 12–6 potentials[14] for the non-bonded interactions among beads.

The beads adjacent along the chain are connected by stiff harmonic bonds whose lengths are determined from the atomic-scale geometry. In addition to this connectivity, and the non-bonded pair potentials, the overall potential also operates on three types of bond angles: c-p-i, c-i-c, and i-c-i. All c-p-i angles are held at 180° by stiff harmonic potentials. The angles defined by c-i-c and i-c-i triples (skipping the bridging phenylene beads) are constrained according to Boltzmann-inverted potentials tabulated via Monte-Carlo averaging over the atomic scale potential. At a specified temperature, the value

of any c-i-c or i-c-i angle is thus constrained to the correct distribution consistent with a canonical average over the atomic scale potential.

The philosophy behind this method of coarse-graining has been discussed previously[6,9]. Briefly, there are three major assumptions used. (1) The coarse-grained degrees of freedom are uncorrelated, allowing us to write a coarse-grained potential with additive contributions from each degree of freedom. (2) The intramolecular potential at the atomic level is not influenced by intermolecular degrees of freedom. This is a safe assumption for most synthetic (carbon-based) polymers at temperatures below those at which thermal decomposition can occur. (3) The intermolecular interactions at the coarse-grained level are approximated to an acceptable level of accuracy by pair-wise repulsive potentials, at least for simulating equilibrium structures.

2.2 Adapting the 4:1 Model for Surface Studies: *Ab Initio* Calculations

The coarse-graining procedure described above yields models which are most appropriately used in bulk simulations. However, it is of interest presently to understand how polymer molecules behave at metal interfaces. We have chosen to consider the specific system of BPA-PC on nickel (111), for the reasons alluded to in the Introduction. What changes must be made to the current 4:1 model, if any, to allow us to use it to study the BPA-PC-Ni interface at the molecular level?

To answer this question, it would be desirable to perform *ab initio* calculations of at least a single BPA-PC molecule in the vicinity of a semi-infinite slab of nickel atoms with a (111) surface arrangement. Were such a simulation tractable, we could use it to determine the exact nature of any specific interactions between any group of atoms in the chain and any group of atoms on the surface. Appropriately averaging over all possible interaction geometries would then yield probability distributions which could be inverted into potentials for use in coarse-grained simulation.

There are two problems here. The first is that the *ab initio* calculations described are impossible based purely on the number of atoms required, with current or even next-generation computing power. The second is, even if they were possible, and even if we could gain enough statistical strength to perform the averages appropriately, we would have to greatly expand the parameter space to consider how specific interactions with the surface alter the *intramolecular* potential of the molecule. Probing all possible conformations and orientations of a chain of even one repeat unit next to a sufficently large slab of nickel using *ab initio* techniques would be a monumental effort.

Our strategy has been to consider first small molecules which correspond to the chemical subunits of BPA-PC[8,11]. This is motivated not only by the need of computational tractability, but also has the important advantage that the subunits we study are also important for polymers other than BPA-PC. We performed Car-Parrinello MD calcuations[15] to predict the interaction energies of each of these molecules with a finite slab of nickel comprised of four atomic layers. Here, we summarize the results. We observed that at all relevant orientations, carbonic acid and propane are strongly repelled from nickel (111) when the distance between center of mass and first layer Ni atoms is below 3 Å. Both benzene and phenol strongly adsorb in a horizontal orientation at a distance of 2 Å from the top layer, with a strength of about 1 eV. This interaction is short-ranged, dying off above 3 Å, and strongly orientationally dependent, decaying nearly to zero if the angle between

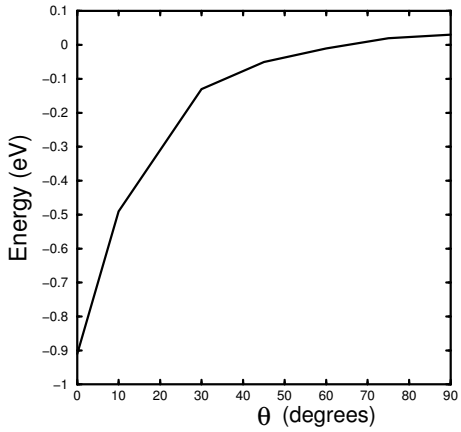

Figure 2. Adsorption energy of phenol at the Ni(111) bridge site as a function of the inclination of the carbon ring with respect to the surface.

the normal of the surface of the ring and the normal of the nickel surface plane deviate in direction by more than about 45°, as depicted in Fig. 2.

The crucial step in incorporating this information into the 4:1 coarse-grained model is to realize two things. First, although internal phenylenes would apparently prefer to stick to the nickel surface, thereby lowering the system potential energy, they are sterically hindered by the strong repulsion felt by the adjacent isopropylidene. Second, the phenoxies at the ends of the chains are not sterically hindered because the carbonate can orient with one bridging oxygen at the surface and the other away, allowing the terminal phenoxy group to strongly bind without steric hindrance. However, the orientation of the ring is a sensitive determinant of the interaction strength, and this degree of freedom does not exist in the bulk 4:1 model.

2.3 The Dual Resolution BPA-PC Model

The solution to this problem is the so-called molecule-fixed dual-resolution model, depicted in Fig. 2. The essential feature of the dual-resolution model is that the terminal *carbonates* are resolved atomically. This is true of all molecules in the system, regardless of their proximity to the surface. We therefore refer to this as a "molecule-fixed" dual-resolution scheme. Instead of using a single c-type bead to represent the outermost carbonates, we use explictly one carbon atom, denoted "C," two bridging oxygen atoms, denoted "O_b," and a single carboxylic oxygen, denoted "O_C." The orientational degree of freedom we must access is determined by a vector joining the outer bridging oxygen of the terminal carbonate group and the center of the terminal phenyl ring. The direction of this vector is the "tilt" of the phenyl ring. Because we know the torsional barriers around this bond to be on the order of thermal energy at T = 570 K, we assume that rotation of the phenyl ring optimizes instantaneously relative to the tilt, and hence, we need only to resolve the carbonate group to access the tilt degree of freedom. Atomic-scale potentials taken from all-atom simulations of liquid diphenyl carbonate[16] are used to enforce all

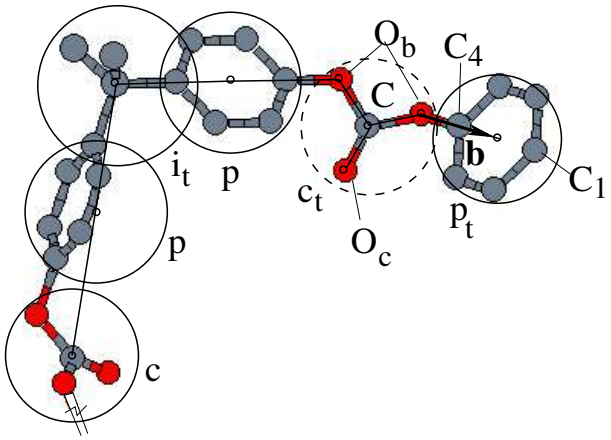

Figure 3. Atomistic structure of a representative chain-end conformation of BPA-PC illustrating the dual-resolution scheme. The small black circles are mapping points in the scheme, and the large circles represent the excluded volume diameters of those points. The C_4-C_1 orientation vector, $\mathbf{b}$, is shown. Lower-case letters denote coarse-grained bead designations: "p" is phenylene, "c_t" is the terminal carbonate, "p_t" is the terminal phenoxy, and "i_t" is the terminal isopropylidene. Capital letters denote atom type designations (see text).

bonds, angles, and the one improper dihedral arising from this group.

The challenge in this dual-resolution scheme, as in any scheme that simultaneously resolves a single system with two or more levels of resolution, is handling the interface between the two levels of resolution. Here, this requires specifying how the inner O_b is bonded to its adjacent phenylene bead and how the outermost O_b is bonded to its adjacent, chain-terminating phenyl, forming the phenoxy end. For this reason, the outermost phenylidene (p in Fig. 2 owns a mapping point tethered to its center of mass, unlike other phenylidenes. Then, the p–O_b bond is enforced at its natural length by a stiff harmonic bond. The same applies for the bond between the outermost O_b and the terminal phenyl p_t.

The p–O_b–C and p_t–O_b–C angles are treated using harmonic potentials as well, as if both the p-type and p_t beads were carbon atoms. The two O_b–C torsional potentials also use the p-type beads as carbon atoms. The angle defined by the outermost isopropylidene, i_t, the inner bridging oxygen, and the carbonate carbon is constrained at its geometrically determined value of 180° using a stiff harmonic potential. Because the outermost phenylene now owns a tethered mapping point, the angle at the outermost isopropylidene is determined by the sequence c–i_t–O_b obeys a different distribution than the normal c–i–c angle, which is computed ahead of time using the same type of Monte-Carlo averaging as in the previous case.

Finally, new intermolecular interactions must be accounted for relative to the previous 4:1 case when the carbonate groups are resolved atomically. However, as a first step, we have chosen the simplest route where the carbon atom is treated in an excluded volume sense as a c-type bead, and the oxygens experience no excluded volume.

The benefit of this new scheme is that the vector connecting the outermost O_b and the terminal phenyl bead determines the orientation of the terminal phenoxy *if* we make the

assumption that a negligble atomic-scale torsional barrier on the O_b-C_4 exists (C_4 is the carbon atom of the phenyl that is bound to the bridging oxygen of the carbonate group). Indeed, this barrier is less than 1 kT at our temperature of interest, which is 570 K[16]. Thus, we can include the orientation of this vector as a degree of freedom upon which we can apply a potential energy, and this allows to accurately account for both the short range and strong orientational dependencies of the phenoxy-nickel interaction. Most importantly, because we are not forced to resolve the entire molecule atomically, we know that no matter how quickly the system responds to the presence of the surface, the chains more than one repeat unit distance from the surface are locally equilibrated, and global equilibration is feasible.

The simulation system is a slit pore, and particles are confined to a central region by the walls. Particle-wall interactions are purely repuslive for internal beads, and are (111)-site-specific and orientationally dependent for the terminal phenoxy beads. The MD simulations are preformed in reduced Lennard-Jones units (1 σ = 4.41 Å) using a time step of 0.005 τ and a Langevin-type thermostat[17] with a friction of 0.5 τ^{-1}. Time is measured in units of $\tau \equiv \sigma\sqrt{m/k_{\mathrm{B}}T}$, where m is the unit mass. Because of the stochastic forces introduced by the thermostats, the masses of the explicit C and O atoms are artifically increased to 1.0 (which is the mass of all beads in the system) to reduce their bond oscillation frequencies. In this sense, using "heavy" carbon and oxygen in the dual resolution scheme is an acceptable alternative to limiting the integration to much smaller time-steps. Our assumption is that using such heavy atoms does not greatly affect the equilibrium structure of the chains or the liquid. The systems were initialized by first growing the chains as phantom random walks in a box with periodic boundaries in all three dimensions. Periodicity was then turned off in the z-dimension, and particle position z-components were unfolded. Walls are then placed at extremes in z and slowly, over 5000 MD steps, brought toward one another until the desired density is acheived.

The results presented in Ref.[11] were extracted from a simulation system of 240 chains, each chain having 10 chemical repeat units. The simulations were run long enough to achieve equilibration, which in this case was assessed by considering the total phenoxy-surface interaction energy. The decay of this energy to its equilibrium value of about 12 $k_{\mathrm{B}}T$ per phenoxy required more than 80,000 τ of integration time for the 10 repeat unit chains. Here, we compare a selection of these results to those from a system of 400 chains, each having 20 chemical repeat units.

3 Dual-Resolution BPA-PC: Results and Discussion

Here we compare a selection of results for chains of 10 and 20 repeat units. The first result we consider is the equilibrium structure and orientation of the chains. As presented in Ref.[11], the chain-end sticking for 10-repeat-unit BPA-PC resulted in a unique two-layered structure in chain packing and orientation as a function of distance from the wall. The dominant length scale in this structure is the unperturbed root-mean-square radius of gyration, R_g, which was about 20 Å for the 10-repeat-unit chains. It was observed that the chains with centers of mass less than about $2R_g$ from the surface were divided clearly into two populations: those with centers of mass between 0 and R_g from the surface (layer I) had both ends adsorbed, while those between R_g and $2R_g$ (layer II) had only one end each adsorbed and were strongly stretched along the direction normal to the wall. This

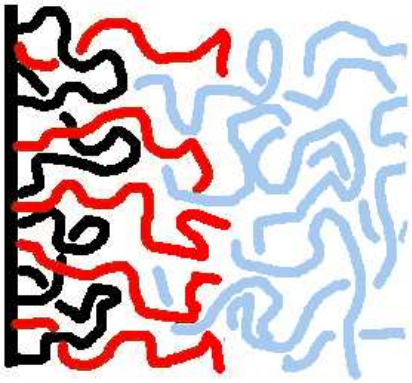

Figure 4. Schematic representation of the molecular structure of a BPA-PC melt adjacent to a Ni wall, showing double-ended adsorbed, single-ended adsorbed, and non-adsorbed chains.

is depicted schematically in Fig. 3. Moreover, the chains in layer I were flattened in the direction z normal to the wall, and chains in layer II were strongly stretched in z. The shapes of the chains are quantified in terms of the zz components of each chain's gyration tensor $\mathbf{S}$, where the trace of this tensor is R_g.

In the case of chains of 20 repeat units, the same general conclusions hold, as shown in Fig. 4. For these chains, R_g is about 29 Å. In Fig. 5(a), we plot both the density of chain centers-of-mass and S_{zz} as functions of distance from the wall, z. At a particular value of z, S_{zz} is the average of all chain S_{zz}'s for chains with centers of mass between z and $z+\delta z$. This data was averaged over the equilibrated configurations with a lateral resolution of δz=0.031 σ. Flattened chains in layer I and stretched chains in layer II are evident. In Fig. 5(b), we show the breakdown of the chains by the number of ends adsorbed. Here we see that most chains in layer I have both ends adsorbed, while most in layer II have only a single end adsorbed. The delineation between populations of chains with single- and double-ended adsorption is not as clear as for the shorter chains, but the same length scaling applies: Those chains with centers of mass less than one bulk R_g from the wall have both ends stuck and are somewhat flattened, while those between one and two R_g have a single end and are stretched. The degree of flattening and stretching is not as pronounced for the 20-repeat-unit chains as for the 10-repeat-unit chains, because each chain has twice as many internal degrees of freedom upon which to call to relieve the stress associated with adsorbing a chain end to the surface while packing densly among other chains.

Finally, because the dual-resolution scheme allows us to ask where the individual C and O atoms of the carbonate groups are located, we can examine atomically resolved depth profiles involving these atoms. Fig. 6 shows the depth profiles of C and O atoms in the terminal carbonate groups, as well as the terminal phenoxy centers of mass, for the chains

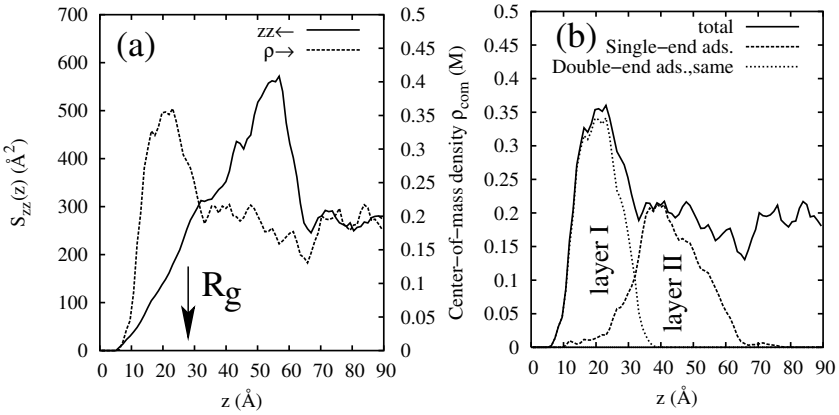

Figure 5. Simulation results for 20-repeat-unit BPA-PC: (a) zz component of the lab-frame mean depth-resolved gyration tensor vs. distance from wall, and chain center of mass density vs. distance from wall. (b) Breakdown of chains into those with single- double-ended adsorption.

with 20 repeat units. We can see that the phenoxy chain ends are tightly localized near the surface. This peak is closely shadowed by one of the two oxygen peaks, populated with those oxygen atoms which are bonded to the phenoxies. Note that the oxygen peak does not lie directly atop the phenoxy peak, as we would expect if all phenoxyies are perfectly horizontal. The separation in these two peaks represents the finite temperature of the system; because of the inhomogeneity in the domain caused by the presence of the inpenetrable surface, thermal fluctuations can only result in a mean orientation that is off-horizontal.

4 On the Development of Domain-Fixed Inhomogeneous Coarse-Graining Schemes: Initial Attempts with Liquid Methane

In the presentation of the molecule-fixed dual-resolution scheme, it should be noted that we have taken advantage of the unique interplay between sterics and energetics for BPA-PC-Ni, requiring that only chain ends be atomically resolved. In principle, one would rather have a technique which would decide for itself what molecular fragments must be atomically resolved and what fragments may remain coarsened, when applied to any particular system with an interface or other interesting structure with atomic resolution in at least one dimension. This would, in effect, be a means to conduct embedded full-blown atomic MD simulations with realistic boundary conditions that optimize on-the-fly. Such ideas are not new in the area of simulations of crystalline materials, where one has the luxury of a reference crystal structure upon which a coarsened mesh can be constructed (for example, Ref.[18]). It is also not new in the area of hybrid quantum/molecular mechanics models (QM/MM), in which a small region of a few atoms is treated quantum mechanically while being embedded in a larger system of atoms treated empirically (for example, Ref.[19]). The idea, however, of "domain-fixed inhomogeneous coarse-graining" for molecular *liquids* is still much more immature. Many unique considerations not yet encountered in other multiresolution techniques must be addressed.

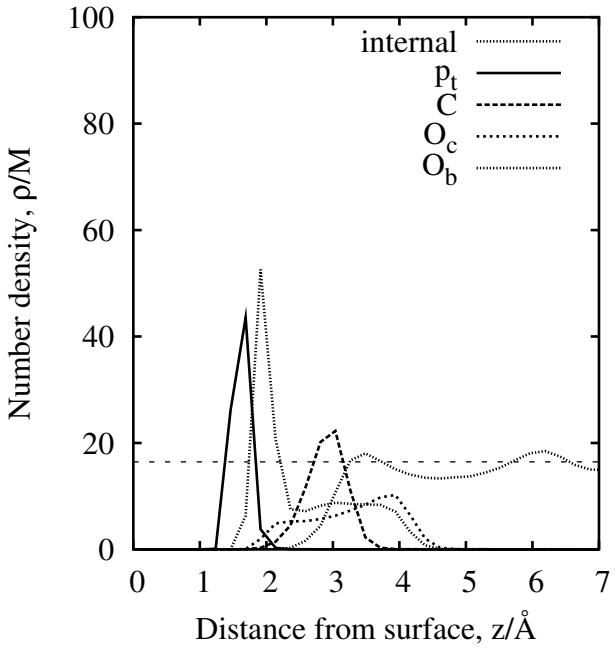

Figure 6. Simulation results for 20-repeat-unit BPA-PC. Depth profiles for atomic constituents in the dual-resolution model.

In this contribution, we discuss attempts to implement a domain-fixed inhomogenously resolved model of liquid methane. Methane was chosen primarily because it is among the simplest polyatomic molecules (CH_4), and has been modeled in simulation studies with both fully atomic resolution (the so-called four- and five-center models) and at a coarsened molecular level (the so-called single-center models)[20]. We wish to examine the following situation. Imagine a box, filled with liquid methane, and divided into two regions whose boundaries are *imaginary and static*; that is, they are not material boundaries. All methane molecules in region I are represented fully atomistically. All methane molecules in region II are represented as single-center coarse-grained particles. Molecules are allowed to move freely between regions; each time a five-center molecule crosses the boundary into region II, it is instantaneously mapped into a single-center molecule with a velocity vector equal to the center-of-mass velocity vector of the molecule. Likewise, each time a single-center particle crosses the boundary into region I, it is "remapped" onto a five-center molecule, each of whose atoms obtains a velocity vector equal to that of the coarse-grained particle. Such a scenario is our attempt at the simplest possible test of domain-fixed inhomogeneous coarse-graining of a dense molecular liquid.

Our first question is, what effects do the presence of these imaginary boundaries between regions of different resolution have on the structure of the liquid? To begin to answer this question, we conducted molecular dynamics simulations of the system described above, composed of 1,000 methane molecules in a box roughly 39 Å on a side, at a temperature of 149.9 K. Reduced Lennard-Jones units are again employed, and the relevant

conversion factors are $\sigma = 3.733$ Å, ϵ = 149.9 K, m = 16 amu (mass of one CH_4). The box is divided in two equal "slabs" by planes normal to the z-axis (the system is periodic, so we need two planes to create two regions). All molecules in slab I are atomistic, and all molecules in slab II are coarse-grained. The single-resolution potentials for methane are taken directly from Ref.[20]. Interactions though boundaries are parameterized using standard Lennard-Jones mixing rules, except that hydrogens in the atomistic region are invisible to coarse-grained particles. The Newtonian equations of motion are augemented by the dissipative particle dynamics thermostat[21,22], with a friction $\zeta = 1.0\ \tau^{-1}$, except for pairs interacting accross a boundary, for which we chose $\zeta = 3.0\ \tau^{-1}$. A single time step of 0.01 τ is employed, although it would have been slightly more efficent to resolve the motion of the coarse-grained particles with larger time steps than the atomistic particles. Several runs from different initial conditions were performed, all exceeding several tens of thousands of time-steps.

We discuss a selection of results here that motivates our introductory discussion of domain-fixed inhomogenous coarse-graining of molecular liquids. Because the imaginary boundaries impart a directionality to the system, it is logical to ask, is the distribution of mass along this direction affected? We show in Fig. 7 that there is indeed a measurable influence of the interface on the distribution of mass in the z-direction. Fig. 7 shows the number density of carbon centers (particle postions in the coarse-grained region, and methane carbons in the atomic scale region) as a function of z. The figure shows the two resolution domains. Clearly, the number density of carbons in both domains should be the same. Note, however, that the density of carbons in the atomic scale region is lower than that in the coarse-grained region. There appears to be some driving force that "pushes" more methanes into the coarse-grained region than should be allowed. The imbalance amounts to about 20 molecules, which is reached within the first few hundred time steps of the simulation.

To understand this apparent artifact, we note first that the two sets of potentials used actually predict different equations of state for methane. The coarse-grained potential, originally due to Saager and Fischer[23], predicts an equilibrium pressure of about 1040 bar (in excellent agreement with experiment) for the state point simulated here. In contrast, the 5-center atomic-scale potential, originally due to Murad and Gubbins[24], predicts an equilibrium pressure almost 60% higher. This higher pressure is likely the reason why particles apparently prefer to occupy the coarse-grained region. Presumably, particles flow into the coarse-grained region until the chemical potential (which to a large degree reflects the pressure) on both sides of the interface is equal. Choosing from among the many other 5-center methane potentials might yield a situation in which this density inhomogeneity disappears. It will be interesting to test whether two potentials which each correctly predict the appropriate state point properties and have the same chemical potential with respect to molecule insertion can be developed and whether they are strictly necessary for this kind of domain-fixed dual-resolution simulation.

5 Conclusions

We have reviewed the "molecule-fixed" dual-resolution representation of BPA-PC used to predict the atomic- and molecular-scale liquid structure at a BPA-PC-Ni interface. The results presented herein complement those that appeared together with the original descrip-

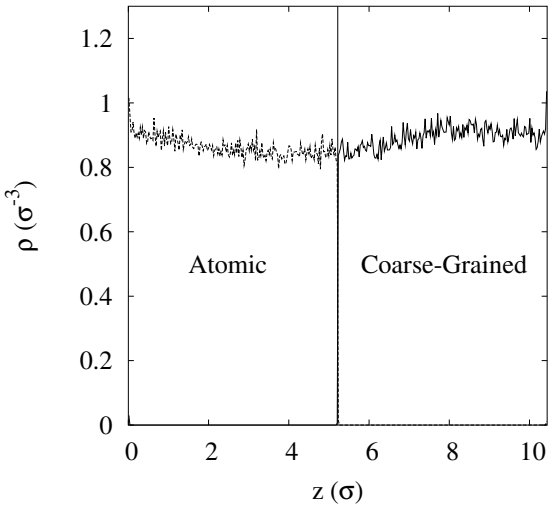

Figure 7. "Depth profiles" of carbon (local number density vs. z position) in both the coarse-grained and atomic scale regions of a domain-fixed dual-resolution simulation of liquid methane. Vertical line denotes boundary between atomically resolved and coarse-grained domains. Average carbon number density is 0.879 σ^{-3}.

tion of the model[11]. Equilibrium chain structure and orientation is qualitatively the same for the two chain lengths considered (10 and 20 chemical repeat units). The liquid structure near the wall is divided into two layers: the outermost layer (immediately adjacent to the wall) contains flattened chains with both ends adsorbed, while the innermost layer (immediately adjacent to bulk liquid BPA-PC) contains stretched chains with single-ends adsorbed.

Our technique of using insight from *ab initio* to construct a minimalistic yet realistic coarse-grained model for a synthetic polymer interacting with a specific metal surface appears to be a promising technique which could be applied to many other specific systems. However, it is recognized that a truly transferable model is one in which the dual-resolution scheme is domain-fixed, and not dependent upon details of the atomic-scale energetics. To this end, we examined some preliminary results of a domain-fixed dual-resolution model of liquid methane as a test case for this kind of simulation. Artifacts due to the presence of the imaginary boundaries between regions of different resolution were discussed.

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